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Liquid Crystalline Macrocycles and Polyacrylates Containing 4-Alkoxybenzoic Acid and 4-Alkoxybenzamide Structural Units

by

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Liquid Crystalline Macrocycles and Polyacrylates Containing 4-Alkoxybenzoic Acid and 4-Alkoxybenzamide Structural Units

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ABSTRACT: The hexa-(4-dodecyloxy)benzamide and hexa-(4-hexyloxy)benzamide derivatives of [18]-N_6 (**2** and **3**), the tetra-(4-dodecyloxy)benzamide derivative of [14]-N_4 (**7**), and a mono-(12-hydroxydodecyl)-penta-(4-dodecyloxybenzoyl) derivative of [18]-N_6 (**5**) have been prepared, and their phase transitions have been determined by DSC and polarizing microscopy. Compounds **2** and **5** have a discotic mesophase. No mesophase was detected for compounds **3** and **7**. The transition temperatures of compound **2** differ substantially from those reported earlier by Lehn, et al., and by DSC **2** exhibits polymer-like thermal history. The 12-hydroxy and 12-acryloxy derivatives of 4-(dodecyloxy)benzoic acid and ethyl 4-(dodecyloxy)benzoate were prepared. Only the carboxylic acids had thermotropic mesophases. Free radical polymerizations of the acrylate monomers gave mesogenic polyacrylates with pendant 4-(12-oxydodecyoxy)benzoic acid and ethyl 4-(12-oxydodecyoxy)benzoate side chains.

Introduction

The optical properties of liquid crystalline materials are both intriguing and useful. Liquid crystals are used in the most common electrooptic displays in calculators and watches, and their nonlinear optical properties may be put to use in the future in new electrooptic devices. Many polymers have liquid crystalline states, and they can be produced as films, glasses, and fibers. Polymeric liquid crystals are of two major types: those with mesogens in the main chain, and those with mesogens in side chains.[1-5] Because the mesogenic units are rigid, the main chain liquid crystalline polymers usually have mesogenic states at high temperature and tend to be fiber-forming.[1-8] Side chain liquid crystalline polymers with flexible backbones and flexible spacer chains connecting the mesogens to the main chain are a subset of branched, comb-like polymers, that often are glassy at low temperature and liquid crystalline at convenient temperatures in the 0-200 ^{o}C range.[1-5,9-13] We have started a program to incorporate unusual mesogenic structures into the side chains of flexible main chain polymers. The aim is to cool polymers that are ordered in higher temperature liquid crystalline states to a glassy state at room temperature with preservation of the liquid crystalline order. The advantages of side chain macromolecular liquid crystals over low molar mass liquid crystals for optical studies are that they may be obtained as transparent, glassy films, and they can be processed as thermoplastics.

The properties of liquid crystals depend on the molecular structures of the mesogenic units and the arrangement of those units in the mesomorphic state. When the mesogenic units are side chains bound to a flexible polymer, their arrangements depend on intra- and intermolecular mesogen interactions, and also on intermolecular interactions with the polymer main chain and the spacer chain and on the conformations of the main chain and the spacer chain. Many rod-like and a few disc-like mesogens have been bound to flexible polymers through flexible spacer chains. Usually the formation of liquid

crystalline phases of comb-like polymers requires at least partial decoupling of the motions of the mesogenic units from the motions flexible main chain of the polymer.

Acyl derivatives of macrocyclic polyamines such as the hexa-(4-dodecyloxy)benzamide derivative **2** of [18]-N_6 (hexacyclen, **1**) have been reported by Lehn, Malthete, and Levelut[14] to form "tubular" mesophases. The mesophase of (**2**) has a hexagonal columnar structure that is pictured with the mesogens stacked such that an open tube passes through the center of each macrocycle.[14] With the long range goal of producing polymer liquid crystals with tubular mesophases, we have prepared **2** and some close relatives of **2** to determine if they also have mesophases. A similar investigation of Mertesdorf[15] indicated that an aromatic ring in the side chains of [18]-N_6 was required to produce mesogenic structures. We also have prepared some monomeric and polymeric derivatives of 4-dodecyloxybenzoic acid that might be used in the synthesis of polymeric relatives of **2**. 4-Dodecyloxybenzoic acid itself has at least one smectic and a nematic mesophase.

Results

Macrocyclic Polyamides. Syntheses. All compounds were characterized by ^1H and ^{13}C NMR spectra and IR spectra, and their purities were tested by thin layer and high performance liquid chromatography. The hexa-(4-dodecyloxy)benzamide and hexa-(4-hexyloxy)benzamide derivatives of [18]-N_6, (**2**) and (**3**), were synthesized from [18]-N_6 and the 4-alkoxybenzoyl chlorides. The mono-(12-hydroxydodecyl) derivative **4** was prepared from equimolar amounts of [18]-N_6 and 12-bromododecan-1-ol. Acylation of **4** gave the monoamine pentaamide derivative **5**. The tetra-(4-dodecyloxybenzoyl) derivative **7** of [14]-N_4 (cyclam, **6**) was prepared by the same method. Compounds **2**, **3**, **4**, **5**, and **7** all showed single peaks by analytical HPLC on normal phase silica.

NMR Spectra. The macrocyclic amides **2**, **3**, **5**, and **7** all had temperature-dependent ^{1}H and ^{13}C NMR spectra. Figures 1 and 2 show spectra of **3**. The aromatic protons at 7.2 ppm and carbons at 129 ppm ortho to the amide function, and the protons and carbons of the macrocycle at 3.7 ppm and 46-50 ppm respectively, give broad signals at room temperature. Those signals are sharper when spectra are recorded at 75 °C, and they show more peaks at -25 °C. Thus the macrocyclic amides **2**, **3**, **5**, and **7** undergo conformational changes on the NMR time scale at room temperature, which can be attributed to hindered rotation about the amide C(O)-N bonds and may also involve conformational changes of the macrocycles. At 75 °C the C-N bond rotations and macrocycle conformational interconversions are fast on the NMR time scale.

Polarizing Microscopy (PM) and Differential Scanning Calorimetry (DSC). The hexa-(4-dodecyloxy)benzamide of [18]-N_6 (**2**) has a mesophase with a texture like that shown by Lehn[14], but the phase transition temperatures agree more closely with those of Mertesdorf[15] than with those of Lehn.[14] Our results in Table I are with a purified sample that shows one peak in HPLC, has an elemental analysis that corresponds with a tetrahydrate, and has ^{1}H and ^{13}C NMR spectra with no detectable impurity peaks. The melting transitions of all of our samples appeared only in the first heating cycle of the DSC thermograms. The mesophase to isotropic transition appeared in second and third heating cycles and in cooling cycles with high precision of ΔH (+0.02 kcal mol^{-1}).

The unsymmetrically substituted derivative of [18]-N_6 (**5**) had a mesophase with the same texture as the mesophase of **2**, and both the melting and the isotropic transition temperatures were lower than those of **2**.

The hexa-(4-hexyloxy)benzamide of [18]-N_6 (**3**) and the tetra-(4-dodecyloxy)benzamide of [14]-N_4 (**7**) had no detectable mesophases. By DSC **7** had two transitions, but no change occurred in the birefingence of the sample at the first transition at 133 °C, and the sample did not form droplets of liquid until the melting transition at 209 °C.

12-Substituted Derivatives of 4-(Dodecyloxy)benzoic Acid. The 12-hydroxy and 12-acryloxy derivatives (**9**)-(**12**) of 4-(dodecyloxy)benzoic acid (**8**) and ethyl 4-(dodecyloxy)benzoate were prepared from ethyl 4-hydroxybenzoate. The side chain carboxylic acid (**13**) and ester (**14**) polymers were prepared by AIBN-initiated polymerizations in benzene solutions. Only the monomeric esters **10** and **12** had no detectable mesophase. We found new monotropic crystalline phases of 4-dodecyloxybenzoic acid, as shown in Figure 3. Carboxylic acids **11** and **13** also were rich in liquid crystal phases, which are reported in Table II. Ten DSC scans were run with acrylic monomer **11** to explore possible polymerization during heating. Each run covered 40-185 °C at a rate of 20 deg min^{-1} followed by cooling in ambient air. Data from the second through fifth runs gave almost the same transition temperatures but inconsistent transition enthalpies. By the tenth run fewer transitions were observed, but the thermogram was still much more like that of fresh **11** than like those of polymer **13**, which showed only one broad transition by DSC on the second run.

Discussion

The phase transition data in Table I for compound **2**, which has a "tubular" mesophase,[14] show how supposedly the same material prepared in three different laboratories can have different properties. Both the transition temperatures and the heats of melting differ. The elemental analyses of our sample fit the composition of a tetrahydrate of **2**, but the ^1H NMR spectrum did not show a water peak. The analyses of **2** fit equally well calaculated values for **2** with four moles of methanol (it was recrystallized from a mixture of ether and methanol) or for **2** and any similar combination of water and methanol. Since the details of sample preparation and purification in the other laboratories are not available,[14,15] we cannot identify any more differences between the samples than those reported here. We did not detect the melting transition in the second and later DSC

scans, as the mesophase supercooled to room temperature. This behavior is common with polymer liquid crystals but is not usually reported for low molar mass materials. Polymeric behavior of **2** is not surprising, because its molecular weight is 1,988.7. Although the transition temperatures differ, our sample had the same microscopic texture as that of Lehn.[14]

Although the mesophase of **2** has been called "tubular," that name is misleading because it implies that the director of the mesophase structure runs through an open tube created by an ordered tube of macrocycles. In the liquid state nature avoids large spaces of free volume. More likely the macrocycle has one or more conformations that leave little or no free volume in the centers. The NMR spectra at 23 and -25 °C in Figures 1 and 2 support complex conformational behavior. The structure has a macrocyclic core surrounded by six long aliphatic chains, as do many discotic mesophases, and we prefer to classify it as a discotic.

Mertesdorf[15] reported that several acyl derivatives of [14]-N_4, including **7**, and the hexa-(dodecanoyl) and hexa-(tetradecanoyl) derivatives of [18]-N_6 had no mesophases, whereas **2** and its hexa(tetradecanoyl) analog each had one mesophase. Our results confirm his, and in addition indicate that a side chain longer than hexyloxy (**3**) is necessary for mesophase formation. Replacement of one of the 4-(dodecyloxy)benzoyl groups with 12-hydroxydodecyl (compound **5**) gave lower transition temperatures but still gave a mesophase. Compound **5** is designed for attachment to a polyacrylate or a polymethacrylate.

Compounds **8**, **9**, and **11** and polymers **13** and **14** show the strong tendency for 4-alkoxybenzoic acids to have several mesophases. Even a strongly hydrogen-bonding substituent, the primary alcohol group of **9**, did not prevent the appearance of a mesophase. Acrylate monomer **11** apparently partly polymerized during repeated DSC scans, for the transition temperatures changed with every scan for ten scans, and the

isotropization temperature of the tenth scan is similar to that observed for polymer **13**, which is a glass at room temperature.

Our results show some problems of reproducibility of the properties of materials such as **2** prepared in different laboratories, most likely due to the difficulty of purification of macromonomeric compounds which tend to behave as polymers during purification and thermal analysis. The replacement of one dodecyloxybenzoyl group of **2** with a 12-hydroxydodecyl group to give **5** provides a precursor to polymeric analogs of **2**.

Experimental Section

N,N-dimethylacetamide (DMA) was freshly distilled from calcium oxide. All other reagents and solvents were used as received unless noted otherwise.

HPLC analyses were performed with a Waters model 590 pump, a Rheodyne injector with either a 200 or a 20 μL sample loop, a normal phase 5 μm silica column (Whatman Partisil 5 for analytical use or Whatman Magnum 9 for semi-preparative use), and a Beckman model 153 analytical 254 nm UV detector fitted with a 10 mm path length flow cell for analytical use or a 2 mm path length cell for semi-preparative use. The eluting solvent was 90/10 v/v chloroform/methanol unless noted otherwise.

^{1}H and ^{13}C NMR spectra were recorded at 300.0 and 75.43 MHz with a Varian XL-300 instrument in $CDCl_3$ with internal Me_4Si reference at 22 °C except when noted otherwise. IR spectra were recorded with a Perkin-Elmer 681 instrument. Polarizing microscopy was performed with a Nikon Optiphot-Pol microscope equipped with an Instec hot stage and mk1 temperature controller which is operated with an Apple IIe computer (Instec. Inc., P.O. Box 7246, Boulder, CO 80306). Photographs were taken with a Nikon N-2000 35 mm single lens reflex camera. Differential scanning calorimetry was performed with a Perkin-Elmer DSC-2C instrument equipped with a model 3600 data station. All data were obtained during heating at 20 deg min^{-1} under a nitrogen atomosphere. The second or

third run is reported unless noted otherwise. Between runs the sample was cooled to less than 30 °C, and no data at <50 °C were considered significant because of unsuitable baselines.

1,4,8,11-Tetra-(4-dodecyloxybenzoyl)-1,4,8,11-tetraazacyclotetradecane (7) (tetra-(4-dodecyloxy)benzamide of [14]-N_4). 4-Docecyloxybenzoyl chloride (DBCl) was prepared by stirring a suspension of 4-dodecyloxybenzoic acid (Aldrich) in benzene with two molar equivalents of oxalyl chloride at room temperature for 4 h. Evaporation of the liquid left a solid (mp 35-36 °C) that was used without purification. ^{1}H NMR: δ 0.88 (t, 3H), 1.27 (m, 16H), 1.46 (m, 2H), 1.78 (m, 2H), 3.96 (t, 2H), 6.86 (d, 2H), 7.27 (br, 2H). ^{13}C NMR: δ 14.1, 22.7, 25.9, 29.0, 29.3, 29.5, 29.6, 31.9, 68.6, 114.6, 125.1, 134.0, 165.0, 166.9.

A solution of 1.0 mmol of [14]-N_4 (cyclam, Aldrich) and 4.0 mmol of 4-(N,N-dimethylamino)pyridine (DMAP, Aldrich) in 5 mL of N,N-dimethylacetamide (DMA) was stirred under argon . A solution of 4.2 mmol of DBCl in 25 mL of DMA was added and the mixture was kept at 95 °C for 48 h. To the cool solution 200 mL of chloroform was added. The solution was extracted once with 5% aqueous HCl and twice with saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and evaporated to give 2.8 g of crude product. Chromatography through 50 g of silica gel gave impurities with 1/1 chloroform/ethyl acetate as eluant, and then with only chloroform as eluant gave 1.36 g of **7**, mp 198-200 °C. ^{1}H NMR: δ 0.88 (t, 12H), 1.27 (m, 64H), 1.46 (m, 8H), 1.78 (t, 8H), 2.09 (br, 4H), 3.49 (br, 8H), 3.75 (br, 8H), 3.96 (t, 8H), 6.86 (m, 8H), 7.27 (m, 8H). ^{13}C NMR: 14.1, 22.7, 26.1, 29.2, 29.4, 29.5, 29.7, 31.9, ca. 46 (br), 68.1, 114.4, 127.5, 128.7, 160.5, 172.3.

1,4,7,10,13,16-Hexa-(4-dodecyloxy)benzoyl-1,4,7,10,13,16-hexaazacyclooctadecane (2) (hexa-(4-dodecyloxy)benzamide of [18]-N_6). A solution of 100 mg of 1,4,7,10,13,16-hexaazacyclotetradecane ([18]-N_6), the acid chloride from 715 mg of 4-dodecyloxybenzoic acid, 0.15 mL of pyridine, and 15 mL of DMA was

stirred for 72 h at 95 °C. A white solid precipitated upon cooling, and 400 mg was isolated by filtration. It was purified by silica gel chromatography using 90/10 v/v chloroform/methanol as eluant. The component of highest R_f was isolated and crystallized from 50/50 methanol/diethyl ether to provide a solid that showed only one peak by HPLC analysis. ^{1}H NMR (50 °C): δ 0.88 (t, rel A 14, 18H), 1.20-1.55 (m, rel A 93, 90H), 1.77 (m, rel a 14, 12H), 3.70 (br s, rel A 23, 24H), 3.96 (t, 12H), 6.82 (d, 12H), 7.21 (br s, 12H). (Relative peak areas are given for signals that did not integrate exactly to the expected number of protons). ^{13}C NMR (50 °C): δ 13.9, 22.6,.26.0, 29.2, 29.4, 29.5,.31.9, 48.0, 68.2, 114.4, 127.1, 128.9, 160.7, 172.2. IR (KBr): 2960, 2920, 2850, 1630, 1605, 1500, 1465, 1425, 1300, 1250, 1170, 1130, 1040, 835, 760 cm^{-1}. See Table I for DSC and microscopy data.

Anal. Calcd for $C_{126}H_{198}N_6O_{12}$: C, 76.09; H, 10.03; N, 4.22. Calcd for $C_{126}H_{198}N_6O_{12}\cdot 4H_2O$: C, 73.47; H, 10.01; N, 4.08. Calcd for $C_{126}H_{198}N_6O_{12}\cdot 4CH_3OH$: C, 73.79; H, 10.07; N, 3.98. Found: C, 73.62; H, 9.93; N, 4.12. The analytical results from samples dried under vacuum at room temperature and at 80 °C for 15 h were the same within +0.2%.

1,4,7,10,13,16-Hexa(4-hexyloxy)benzoyl-1,4,7,10,13,16-hexaazacyclooctadecane (3). 4-Hexyloxybenzoyl chloride (HBCl) was prepared by the method used for DBCl. ^{1}H NMR: δ 0.9 (t, 3H), 1.4 (m, 4H), 1.5 (m, 2H), 1.8 (m, 2H), 4.05 (t, 2H), 7.0 (d, 2H), 8.1 (d, 2H). ^{13}C NMR: δ 14.0, 22.6, 25.6, 28.9, 31.5, 68.6, 114.6, 125.2, 134.0, 165.0, 167.1. IR (neat): 2940, 2870, 1765 and 1740 br, 1600, 1570, 1505, 1465, 1420, 1390, 1375, 1315, 1265, 1210, 1165, 1120, 1015, 935, 875, 840, 805, 730, 660, 645, 620, 610 cm^{-1}.

A solution of 130 mg (0.50 mmol) of [18]-N_6, 725 mg (3.0 mmol) of HBCl, 370 mg (3.0 mmol) of DMAP, and 20 mL of DMA was stirred for 42 h at 90 °C. A white precipitate of DMAP-HCl was filtered out. The filtrate was mixed with chloroform, extracted twice with 25 mL of 10% HCl, washed with saturated NaCl, dried over

anhydrous $MgSO_4$, and evaporated to 700 mg of a viscous oil which solidified upon standing. The product (500 mg) of was chromatographed through 75 g of neutral alumina with dichloromethane to remove less polar impurities and with 2% ethanol in dichloromethane to elute **3**, 450 mg (62%) of white solid, mp 109 °C (DSC), which showed one peak by HPCL analysis. ^1H NMR ($CDCl_3$, 75 °C): 0.91 (t, 12H), 1.34 (m, 18H), 1.46 (t, 12H), 1.77 (t, 12H), 3.70 (br s, 24H), 3.96 (t, 12H), 6.82 (d, 12H), 7.21 (d, 12H). ^{13}C NMR ($CDCl_3$, 80 °C): 13.7, 22.5, 25.7, 29.2, 31.5, 48.0 (br), 68.4, 114.7, 127.5, 128.9, 160.8, 172.2. NMR spectra at three temperatures are in Figure 1.

1-(12-Hydroxydodecyl)-1,4,7,10,13,16-hexaazacyclooctane (12-hydroxydodecyl-[18]-N_6) (**4**). A solution of 258 mg (1.0 mmol) of [18]-N_6 in 100 mL of THF (distilled from potassium) was warmed to 40 °C under argon, and 2 g of powdered cesium carbonate (Aldrich, 99.9%) was added. To the stirred, refluxing mixture 240 mg (0.90 mmol) of 12-bromo-1-dodecanol (Aldrich) in 100 mL of dry THF was added dropwise over 6 h. The mixture was refluxed 48 h. The cooled mixture was extracted with dichloromethane, and the insoluble carbonate was extracted further with hot chloroform. From the combined, dried organic extracts a white solid was isolated. The solid was insoluble in petroleum ether, carbon tetrachloride, and ethyl acetate, slightly soluble in acetone, benzene, and acetonitrile, and soluble in methanol, ethanol, chloroform, and dichloromethane. This sample of **4** was used directly for the preparation of **5**. ^1H NMR ($CDCl_3$, 50 °C): δ 1.3 (br, 14H), 1.4 (br, 2H), 1.55 (br, 2H), 2.38-2.90 (m, 30H), 3.60 (t, 2H) (calcd relative areas are 18:2:2:2:27:2). ^{13}C NMR (Me_2SO-d_6): δ 25.2, 26.8, 28.8, 32.2, 47.1, 61.3.

1-(12-Hydroxydodecyl)-4,7,10,13,16-penta-(12-dodecyloxy)benzoyl-1,4,7,10,13,16-hexaazacyclooctadecane (**5**). A solution of 320 mg (0.72 mmol) of **4**, 3.62 mmol of 4-(dodecyloxy)benzoyl chloride, 0.3 mL of DMAP, and 15 mL of DMA was stirred under argon for 72 h at 95 °C. Removal of the solvent under reduced pressure left a mixture of solids. The solids were extracted into

dichloromethane, washed with 10% NaOH and with water, dried over anhydrous sodium sulfate, and evaporated to yield 1.2 g of an oil which solidified upon standing. The product (1.1 g) was chromatographed over 100 g of basic alumina. Elution with 150 mL of 3% methanol in dichloromethane gave 930 mg (85%) of recovered solid in four fractions. On silica gel TLC this compound has an R_f of 0.8 with a long tail when developed in 5% methanol in dichloromethane. NMR spectra showed that the second fraction had the highest content of **5**, but even it contained two components of R_f 0.4 and 0.0 on silica gel TLC with chloroform. This fraction was flashed chromatographed over silica gel. The desired **5** eluted with 90/10 v/v chloroform/methanol. HPLC analysis showed one peak with a shoulder of lesser retention volume that comprised less than 10% of the peak area. DSC and microscopy results are in Table I. ^{1}H NMR ($C_2D_2Cl_4$, 80 °C): δ 0.85 (t, 15 H), 1.3 (br s, 94H), 1.4 (m, 11H), 1.75 (m, 13H), 3.58 (t, 2H), 3.65 (br s, 18H), 3.97 (t, 2H), 4.24 (t, impurity, about 2H), 6.82 (m, 10H), 7.92 (d, impurity, about 1H). ^{13}C NMR ($CDCl_2CDCl_2$, 100 °C): δ 15.2, 23.9, 27.3, 30.3, 30.5, 30.6, 30.7, 30.9, 33.2, 49.2, 59.3, 49.7, 66.1, 69.2, 78.6 (imp.), 101.1 (imp), 115.8, 116.1, 128.8, 130.2, 130.3, 132.8 (imp) 136.6 (imp), 162.2 (imp), 164.2 (imp.), 167.6 (imp), 173.4. The impurity peaks comprised about 10% of the total peak heights of the spectrum. IR (KBr): 3450 (no OH peak distinguishable in either KBr or Nujol spectra), 2920, 2850, 1715, 1655, 1640, 1625, 1575, 1510, 1470, 1430, 1250, 1175, 1110, 1080, 1090, 1080, 840, 765, 720 cm^{-1}.

Ethyl 4-(12-hydroxydodecyloxy)benzoate (10). Ethyl 4-hydroxybenzoate was prepared by *p*-toluenesulfonic acid-catalyzed esterification of 10.3 g of 4-hydroxybenzoic acid and 3.9 mL of ethanol in benzene: yield 7.3 g, mp 103-104 °C. A sodium ethoxide solution was prepared from 575 mg (25 mg-atom) of sodium in 200 mL of ethanol under argon. Ethyl 4-hydroxybenzoate, 4.15 g (25.0 mmol), and 5.13 g (20.0 mmol) of 12-bromo-1-dodecanol were dissolved in the ethanolic solution. The solution was refluxed 24 h. Solvent was evaporated, and the residue was extracted with 250 mL of

chloroform. The solution was washed with 10% HCl, 10% NaOH, and water, dried over anhydrous magnesium sulfate, and evaporated to yield 6.715 g (96%) of an oil of **10** that crystallized on cooling; mp 34-36 °C. ^{1}H NMR: δ 1.2-1.5 (m, obsd area corresponded with more than the expected 19H, but there is no other sign of impurities), 1.8 (m, 4H), 3.7 (t, 2H), 4.05 (t, 2H), 4.6 (q, 2H), 6.95 (d, 2H), 8.05 (d, 2H). IR (KBr): 2920, 2850, 1715, 1610, 1510, 1470, 1370, 1315, 1280, 1255, 1170, 1105, 1030, 845, 770, 695, 645 cm^{-1}.

4-(12-Hydroxydodecyl-1-oxy)benzoic Acid (9). Saponification of 3.0 g of **10** gave 2.75 g of crude **9**, which was dissolved in 10% NaOH, washed with chloroform, acidified to pH 1, extracted into a mixture of benzene and ethyl acetate, and dried to give 1.5 g of white solid **9**. For DSC and microscopy results see Table II. ^{1}H NMR (Me_2SO-d_6): δ 1.3 (m, 16H), 1.4 (m, 2H), 1.7 (m, 2H), 3.4 (t, 2H), 4.0 (t, 2H), 7.0 (d, 2H), 7.9 (d, 2H). ^{13}C NMR (Me_2SO-d_6) δ 25.5, 28.6, 28.8, 28.9, 29.0, 29.2, 32.6, 60.7, 67.7, 114.1, 123.4, 131.3, 162.1, 167.2. IR (KBr): 3300, 2930, 2860, 1705, 1615, 1520, 1475, 1425, 1390, 1310, 1265, 1225, 1175, 1115, 1040, 850, 780, 640 cm^{-1}.

Ethyl 4-(12-acryloxydodecyl-1-oxy)benzoate (12). A solution of 700 mg (1.79 mmol) of **10** and 0.2 mL of triethylamine in 12 mL of benzene was cooled to 5 °C, and 200 mg (2.21 mmol) of acryloyl chloride was added with stirring. A white precipitate formed quickly. The mixture stirred 4 h after warming to room temperature. The benzene filtrate was washed with water, dried with anhydrous magnesium sulfate, and evaporated to 300 mg of colorless oil which crystallized after scratching: mp 35 °C. ^{1}H NMR ($CDCl_3$): δ 1.3-1.5 (m, 18H), 1.6 (m, 2H), 1.8 (m, 2H), 3.4 (t, 2H), 4.0 (t, 2H), 4.35 (q, 2H), 6.9 (d, 2H), 8.0 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 14.3, 25.8, 25.9, 28.5, 29.0, 29.2, 29.4, 60.4, 64.5, 68.0, 113.9, 122.5, 128.5, 130.3, 131.4, 162.7, 166.2. IR (neat): 2930, 2860, 1720, 1605, 1510, 1470, 1410, 1370, 1280, 1255, 1195, 1170, 1105, 1060, 1025, 985, 855, 810, 770, 720, 700, 645 cm^{-1}.

4-(12-Acryloxydodecyl-1-oxy)benzoic Acid (11). A solution of 500 mg (1.38 mmol) of **9**, 10 mL (146 mmol) of acrylic acid (Aldrich, distilled under vacuum and stored at 5 °C), 0.8 g of hydroquinone, and 0.8 g of *p*-toluenesulfonic acid in 20 mL of toluene was heated to reflux over night. The cool mixture was washed with 3 x 25 mL of water and evaporated. The recovered solid was triturated in hot water, filtered, washed with cool water and with 5 mL of methanol, and dried under vacuum to leave 300 mg of white solid that showed only one component on TLC. DSC and microscopy results are reported in Table II. ^{1}H NMR ($CDCl_3$): δ 1.3 (m 16H), 1.67 (m, 2H), 1.81 (m, 2H), 4.02 (t, 2H), 4.15 (t, 2H), 5.81 (d, J = 11.1 Hz, 1H), 6.12 (dd, J = 16.9, 11.1 Hz, 1H), 6.40 (d, J = 16.9 Hz, 1H), 6.93 (d, J = 8.6 Hz, 2H), 8.06 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 25.9, 28.6, 29.1, 29.2, 29.3, 29.5, 64.7, 68.2, 114.2 (aromatic meta to COOH), 121.4 (aromatic ipso to COOH), 128.6 (vinyl), 130.5 (vinyl), 132.3 (aromatic, ortho to COOH), 163.6 (aromatic bound to O), 171.9 (carbonyl). IR (KBr): 3600-2500 br, 2920, 2845, 1720, 1675, 1605, 1575, 1510, 1475, 1430, 1410, 1250, 1200, 1170, 1030, 990, 980, 840, 810, 770, 640 cm^{-1}. (All bands at <1000 cm^{-1} were weak).

Poly[4-(12-Acryloxydodecyl-1-oxy)benzoic Acid] (13) was prepared in benzene solution at 75 °C with three portions of 2 mol % of AIBN initiator added over a period of 48 h. The polymer precipitated from benzene was recovered in low yield. The polymer was soluble in methanol. The same method was used to prepare poly[ethyl 4-(12-acryloxydodecyl-1-oxy)benzoate] (**14**).

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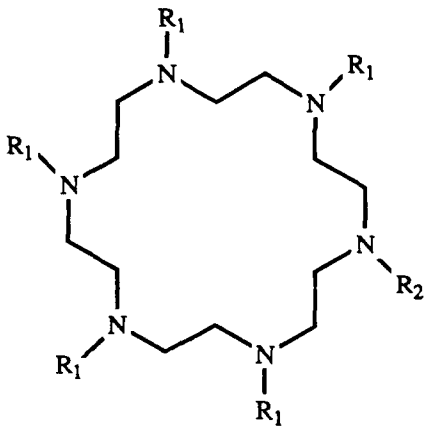
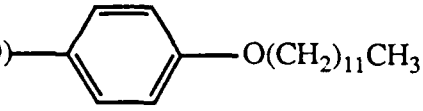
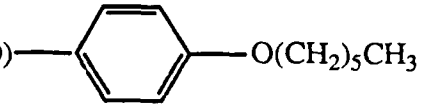


1: $R_1 = R_2 = H$

2: $R_1 = R_2 = C(O)$–  –$O(CH_2)_{11}CH_3$

3: $R_1 = R_2 = C(O)$–  –$O(CH_2)_5CH_3$

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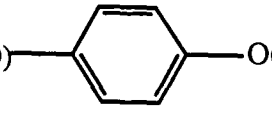
5: $R_1 = C(O)$–  –$O(CH_2)_{11}CH_3$

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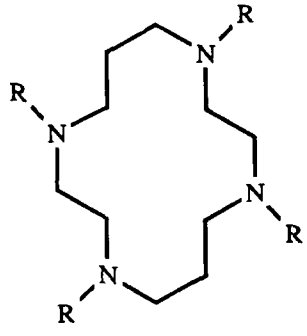
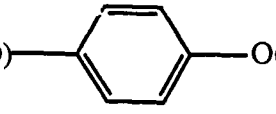
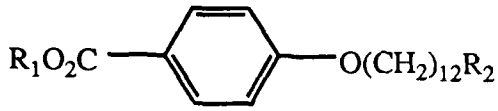


6: $R = H$

7: $R = C(O)$–  –$O(CH_2)_{11}CH_3$



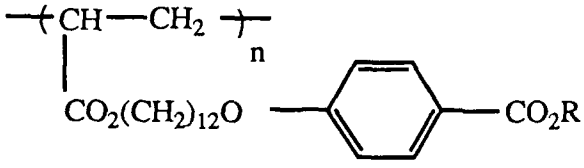
8: $R_1 = R_2 = H$

9: $R_1 = H$, $R_2 = OH$

10: $R_1 = C_2H_5$, $R_2 = OH$

11: $R_1 = H$, $R_2 = O_2\,CCH = CH_2$

12: $R_1 = C_2H_5$, $R_2 = O_2\,CCH = CH_2$



13: $R = H$

14: $R = C_2H_5$

Table I. Phase Transitions of Macrocyclic Amides.

compound	expt	transitions, °C (ΔH, kcal mol^{-1})[a]
2[b]	PM	C 105 M 134 I
2[b]	DSC	C 102 (30.4) M (0.65) 131 I
2[c]	DSC	C 121.5 (37.5) M 141.5 (0.7) I
2[d]	DSC	C 108 (25.4) M 140 (0.6) I
3	DSC	C 109 I
5	PM[e]	C 75 M 105 I
5	DSC[f]	C 65 M 95 I
7	DSC	C_1 133 (6.6) C_2 209 (15.2) I

[a]C = crystal, M = mesophase, I = isotropic. [b]This work. [c]Data from Lehn.[14] [d]Data from Mertesdorf.[15] [e]Transitions observed repeatedly. [f]Transitions observed only on first scan.

Table II. Phase Transitions of 4-(Dodecyloxy)benzoic Acid and Its 12-Substituted Derivatives.

compound	expt	transitions, °C (ΔH, kcal mol^{-1})[a]	source
8	PM	See Figure 3.	
8	DSC	C_1 67 C_2 89 S 129 N 135 I	
8	PM	C_1 83 C_2 90 S 133 N 139 I	Herbert[16]
8	DSC	C_1 73 C_2 86.5 S 132 N 137.5 I	Sternberg[17]
8	PM	C 95 S 129 N 137 I	Gray[18]
9	PM[c]	C 108 M_1 115 M_2 133 I	
11	PM	C 86 M_1 93 M_2 106 M_3 114 I	
11	DSC[d]	C_1 57 C_2 71 M_1 79 M_2 104 M_3 134 I	
11	DSC[e]	C 55 M_1 99 M_2 125 I	
13	PM	G 75 M_1 88 M_2 117 I	
13	DSC	M 127 I[f]	
14	DSC	g	

[a]C = crystal, S = smectic, N = nematic, M = unidentified mesophase, G = glass, I = isotropic. [b]Data from ref. [c]Other mesophases were observed during cooling but were not explored carefully. [d]Fourth heating cycle. [e]Tenth heating cycle. [f]One broad transition 57-127 °C. [g]A broad exotherm was centered at 120 °C during the first heating run. No transitions were observed in subsequent runs.

Figure Captions

Figure 1. ^{1}H NMR spectra of hexa-(4-hexyloxybenzamide) **3**. Peaks marked x are due to a trace of N,N-dimethylacetamide.

Figure 2. ^{13}C NMR spectra of **3**.

Figure 3. Phase transitions of 4-dodecyloxybenzoic acid (**8**) observed by polarizing microscopy.

Figure 1

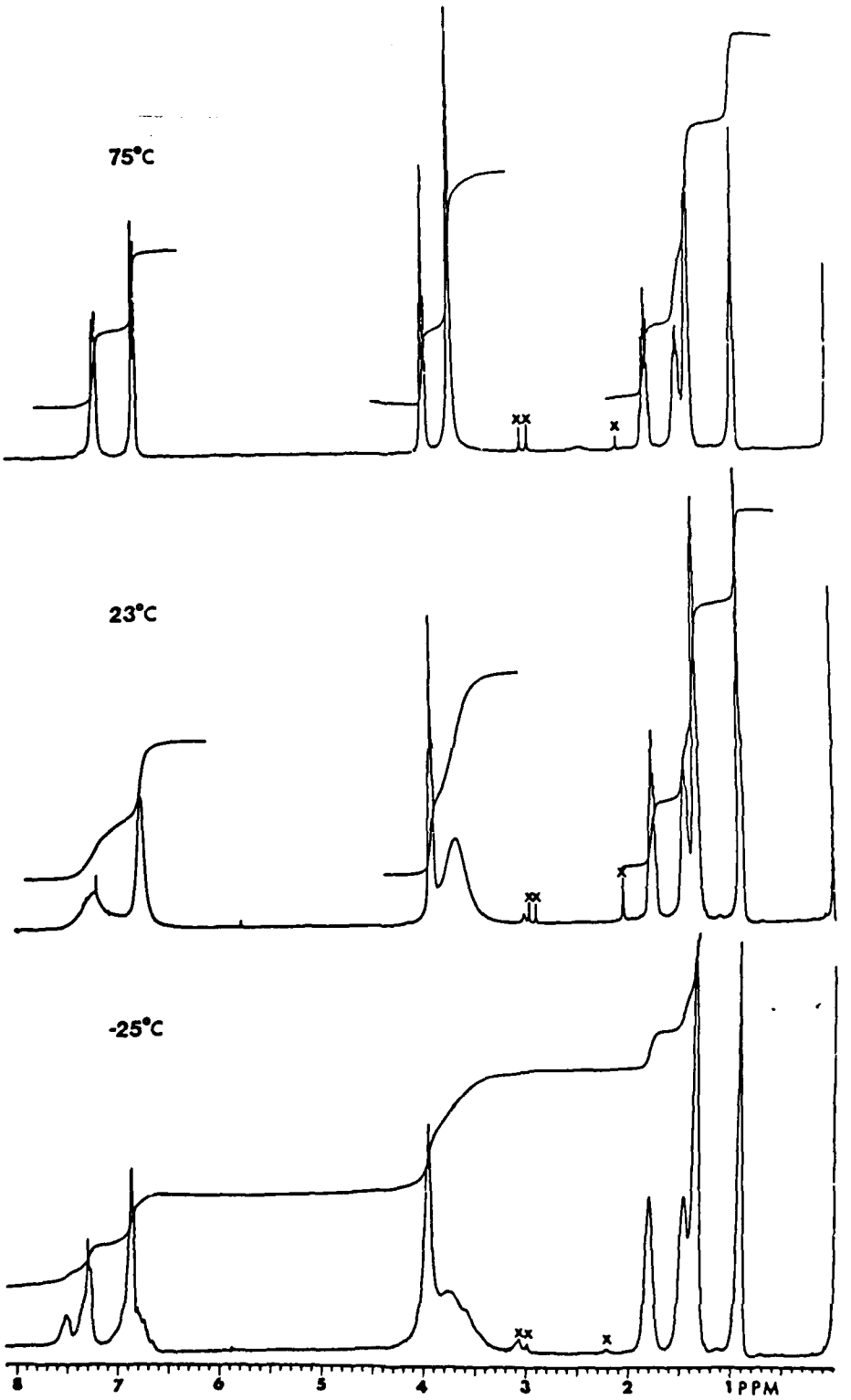


Figure 2

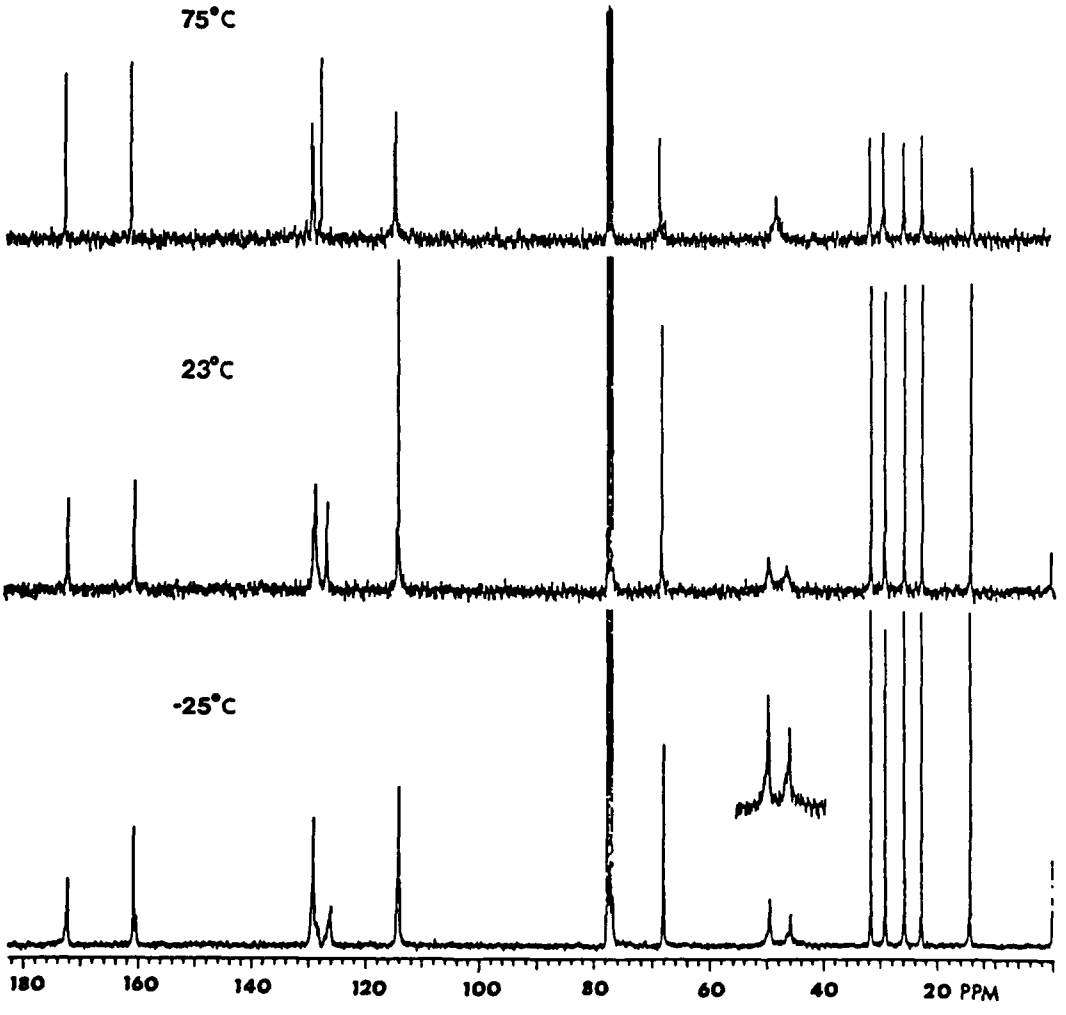


Figure 3